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Kinetics and Selectivity of 2-Propanol Conversion on Oxidized Anatase TiO_2

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The steady-state kinetics of 2-propanol decomposition on oxidized anatase TiO_2 have been determined at temperatures ranging from 448 to 598 K and 2-propanol partial pressures from 8.9 to 102.7 Torr. The effects of the addition of O_2 and water to the carrier gas were also investigated. The steady-state reaction results primarily in the formation of a dehydration product, propylene, and a dehydrogenation product, acetone, with small amounts of carbon oxides also being observed. Depending on the reaction conditions, the selectivity to either propylene or acetone can range between 5 and 95%. The rate of dehydrogenation increases dramatically with the addition of both O_2 and water, while the dehydration rate is unaffected by their presence. Accordingly, the kinetics of 2-propanol decomposition were investigated using both air and an inert carrier. Using air as the carrier gas, the dehydration and dehydrogenation reactions were determined to be approximately one-half order with respect to 2-propanol partial pressure. The activation energies determined for the two processes are substantially different, 68 kJ mol^{-1} for dehydrogenation and 130 kJ mol^{-1} for dehydration, as evidenced by the strong temperature dependence of the decomposition selectivity. Using an inert carrier, the reaction kinetics depend in a complex fashion on the conversion of 2-propanol. The dependence on conversion was found to arise from the influence of water on the dehydrogenation kinetics. The presence of water, whether produced by 2-propanol dehydration or added independently, was found to increase the rate of 2-propanol dehydrogenation. The results of the present study can be reconciled with previously reported steady-state and temperature-programmed desorption investigations of 2-propanol on TiO_2 by recognizing the influence of both surface hydroxyls and the use of an oxidizing carrier gas on the dehydrogenation and dehydration pathways at steady state. © 1997 **Academic Press, Inc.**

INTRODUCTION

The existence of empirical correlations between acidic properties and activities of catalysts for acid-catalyzed reactions has been well documented (1). It is therefore enticing to be able to characterize the properties of materials by using simple probe reaction chemistries. The adsorption and reaction of alcohols on metal oxide surfaces has been used as one such probe (2) and, as a result, has been studied extensively utilizing a wide variety of experimental techniques including infrared spectroscopy (3–5), temperature-programmed desorption (TPD) (3, 4, 6) and steady-state kinetic methods (7–16), microcalorimetry (17, 18), and ultra-high vacuum surface science (19–23). In particular, 2-propanol decomposition on metal oxide surfaces has been employed frequently as a probe of surface acid–base properties (8, 11, 14, 15, 24–32). The dehydration to propylene is assumed to proceed at acidic sites, while dehydrogenation to acetone is presumed to be catalyzed, in a concerted fashion, by both acidic and basic sites (27, 33). The acidic and basic properties of a wide variety of metal oxides, as determined by the relative rates of dehydration and dehydrogenation of 2-propanol, have been correlated with activity and selectivity changes for a number of acid- and base-catalyzed reactions (27, 29, 32).

Despite its frequent application as a chemical probe of surface properties, considerable disagreement exists over the absolute and relative rates of dehydration and dehydrogenation on a number of simple metal oxide materials, including TiO_2. For example, Gervasini and Auroux (8) and Cunningham *et al.* (34) both studied the decomposition of 2-propanol on samples of anatase TiO_2 at equivalent conditions of temperature, total and partial pressure. Comparison of the reported rates per unit surface area for dehydration and dehydrogenation show differences of nearly two orders of magnitude for dehydration and over two orders of magnitude for dehydrogenation. The ratio of dehydrogenation to dehydration, reported to be the important parameter in determining the basic properties of the catalyst (8), differs by approximately a factor of three between the two investigations.

Such differences could largely be explained by the use of different samples, and possibly different purities and contaminants, between the two research groups. For example, Cunningham *et al.* (34) studied 2-propanol decomposition on three different TiO_2 samples and found rates varying by 1-2 orders of magnitude for both dehydration and dehydrogenation paths, with no clear dependence on bulk crystal structure or oxide source. However, both Bond and Flamerz

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(9) and Cunningham *et al.* (34) studied 2-propanol decomposition on the same commercial sample of TiO_2 (Degussa, P-25). While the dehydration rate was comparable in both investigations, the rate of dehydrogenation was insignificant in the work of Bond and Flamerz, while Cunningham *et al.* had a substantial dehydrogenation rate and resulting acetone selectivity (96%). If the dehydration and dehydrogenation rates are taken as indicators of surface properties, the acid-base properties determined for this material by two different groups are in complete opposition. Presumably, the common TiO_2 sample used by the two groups could not itself be responsible for such considerable differences in catalytic properties, and an alternative explanation must be sought. In part because of this variability of observed rates, a detailed interpretation of the kinetics of 2-propanol decomposition on most metal oxides is not presently available. Such fundamental understanding would seem essential in order to confidently utilize the results of this or any probe reaction for catalyst characterization purposes.

In this contribution, we begin a systematic investigation of the kinetics of 2-propanol decomposition on anatase TiO_2, with particular emphasis on the relative and absolute rates of dehydration and dehydrogenation and their dependence upon typical experimental variables. As both air and helium are often used as carrier gases in alcohol reaction studies on metal oxides, we have investigated the effect of carrier gas composition on the activity and selectivity during 2-propanol decomposition. The steady-state decomposition products of 2-propanol were composed of a relatively simple combination of dehydration and dehydrogenation products, with minor contributions at selected conditions from complete oxidation and bimolecular ether formation reactions. A strong dependence of the relative rates of dehydrogenation and dehydration on the chosen reaction conditions was observed. The two factors which largely control selectivity are the reaction temperature and the presence or absence of O_2 in the reaction mixture, with the rate of dehydrogenation being particularly dependent upon the latter. Variations in these two experimental parameters among different research groups are most likely responsible for the apparent discrepancies in previous reports. Water was also found to have an important effect on the reaction selectivity, as described below.

EXPERIMENTAL

Steady-state kinetic investigations were performed in a typical quartz microreactor flow system at atmospheric pressure. The apparatus consisted of three sections. In the first section, mass flow control valves regulate the flow of gases into a manifold, allowing mixtures of gases to be admitted to the reactor. Liquid reactants, in this case 2-propanol (Sigma-Aldrich, HPLC Grade, 99.5%), are mixed into the manifold gas stream by saturation of the gas with liquid held in a constant temperature bath. The bath was maintained at constant temperature using a MGW/Lauda RM6 thermostated bath containing either a 50/50 mixture of methanol and water or water, depending on the temperature desired. Sufficient gas-liquid contact time is necessary to achieve reproducible partial pressures of liquid reactant by this method. Accordingly, only a narrow range of gas flow rates through the saturator were used in this study, and the alcohol partial pressures were verified for saturation against an absolute standard via gas chromatography.

The reactor was a 25-cm-long, 6-mm-diameter quartz tube which was flared to 13 mm in the center over a distance of 2 cm. This middle section of the reactor holds the catalyst particles, sandwiched between two plugs of quartz wool which had been washed with warm nitric acid and baked at 773 K for 24 h. The wall of the reactor is indented into the center of the catalyst bed for insertion of a thermocouple probe for measurement of the bed temperature. The reactivity of all catalyst-supporting materials was tested at all flow rates and partial pressures used in this study; conversion due to support materials was always less than 0.02%.

The analysis section consisted of two on-line sample valves with additional flow switching valves within a Hewlett-Packard 5890 Series II Plus gas chromatograph to allow simultaneous injection and analysis for C_1 to C_{10} hydrocarbons and oxygenates, permanent gases and water. Analyses for hydrocarbons and oxygenates were carried out on a 100 meter, 0.25 mm o.d. HP-1 capillary column using a flame ionization detector. Permanent gases and water were completely separated by sequencing the analysis on two 1/8 in stainless steel packed columns, an 8 ft HaySep Q column and a 10 ft molecular sieve 13X column, and were detected by a thermal conductivity detector. Switchable valves allowed analysis of the gas stream either immediately following or prior to the reactor, providing a precise determination of the reactor feed composition as well.

A commercially available anatase titanium dioxide (Aldrich, BET surface: 10.0 m^2/g) was used in this work. In several cases, the kinetics results obtained with this sample were compared to two other anatase titanium dioxide samples (Fisher Scientific, 10.1 m^2/g; American Instruments, 10.3 m^2/g). The rates and kinetic behavior were found to be nearly identical with all three samples. Pretreatment of the titanium dioxide, performed in the reactor system, consisted of heating the catalyst sample to 673 K in 50 cm^3/min dry air (Matheson) and oxidizing for 2 h. After oxidation, the sample was cooled to the temperature of interest in 50 cm^3/min dry air. When the temperature became stable at the desired reaction temperature, the flow was switched to the carrier gas. Carrier gas streams consisting of dry air (Matheson), high-purity helium (Matheson, 99.999%) and 0–20% oxygen (Matheson, Extra Dry) mixed with high-purity helium have been used in this study.

The stability of each catalyst was verified using the minimum carrier flow rate, maximum 2-propanol partial pressure, and both the highest and lowest temperatures for a minimum of 48 h, during which time no change in activity was observed. These tests were repeated for each combination of carrier gas mixture and catalyst. During collection of the kinetic data, each catalyst was used for no more than 36 h on-stream time before regeneration in air at 673 K. Amounts of catalyst were varied between 0.1 and 0.7 g, depending on the conversion desired at a given set of reaction conditions.

RESULTS

1. *Dry Air as 2-Propanol Carrier*

The reaction of 2-propanol on oxidized titanium dioxide in dry air results in products from dehydrogenation, dehydration and complete oxidation reaction pathways. The selectivity of each pathway depends significantly on reaction temperature but only weakly on conversion. Conversion data and selectivity to carbon-containing products for temperatures from 448 to 598 K and a 2-propanol partial pressure of 8.9 Torr are presented in Table 1. The product

TABLE 1

Conversion, Selectivity, and Rate of Reactant Consumption and Product Formation for 2-Propanol Decomposition on Oxidized Anatase TiO_2 at a Partial Pressure of 8.9 Torr, Using Air as the Carrier

T (K)	Conv. (%)	Selectivity			Rate of formation (s^{-1})			Rate of consumption (s^{-1})
		C_3H_6	CO_2	$(CH_3)_2CO$	C_3H_6	CO_2	$(CH_3)_2CO$	$(CH_3)_2CHOH$
448	0			100			2.73×10^{-5}	2.73×10^{-5}
	0.34			100				
	1.89			100				
	4.30			100				
	6.17			100				
473	0	1.3		98.7	1.1×10^{-6}		7.64×10^{-5}	7.75×10^{-5}
	0.29	1.2		98.8				
	1.81	1.0		99.0				
	3.71	1.0		99.0				
	5.89	0.9		99.1				
498	0	2.9	0.0	97.1	5.57×10^{-6}		1.86×10^{-4}	1.92×10^{-4}
	0.31	2.8	0.0	97.2				
	1.95	2.7	0.1	97.2				
	3.91	2.5	0.1	97.4				
	5.78	2.3	0.1	97.6				
523	0	6.3	0.5	93.2	3.02×10^{-5}	2.40×10^{-6}	4.46×10^{-4}	4.79×10^{-4}
	0.41	6.1	0.5	93.4				
	2.17	5.8	0.5	93.7				
	4.05	5.3	0.5	94.2				
	5.77	4.4	0.5	95.1				
548	0	12.1	3.0	84.9	1.00×10^{-4}	2.48×10^{-5}	7.03×10^{-4}	8.28×10^{-4}
	0.32	12.0	3.1	84.9				
	1.75	11.9	3.1	85.0				
	4.24	10.1	3.2	86.7				
	6.00	9.7	3.2	87.1				
573	0	21.0	3.1	75.9	3.76×10^{-4}	5.55×10^{-5}	1.36×10^{-3}	1.79×10^{-3}
	0.28	20.7	3.2	76.1				
	1.96	22.3	3.4	74.3				
	4.17	19.5	3.0	77.5				
	6.27	18.7	2.9	78.4				
598	0	29.3	3.1	67.6	1.28×10^{-3}	1.35×10^{-4}	2.95×10^{-3}	4.37×10^{-3}
	0.45	29.0	3.4	67.6				
	2.17	28.7	4.0	67.4				
	5.09	29.0	5.0	66.0				
	6.89	26.4	4.9	68.7				

Note. Turnover frequency (tof) calculated based upon 2-propanol saturation coverage of 2.22 molecules per nm^2 (6).

TABLE 2

Typical Mass and Atom Balance for 2-Propanol Decomposition Reaction on Anatase TiO_2 Using Air as the Carrier

Inlet		Outlet					
O_2	$(CH_3)_2CHOH$	O_2	$(CH_3)_2CHOH$	H_2O	$(CH_3)_2CO$	C_3H_6	CO_2
10.340	1.149	10.315	1.078	0.0216	0.0652	0.0020	0.0008
C	0.6894	C	0.6892				
H	0.1532	H	0.1534				
O	10.646	O	10.640				
Total	11.4890	Total	11.4826				

Note. All values are mg per minute. Conditions: 523 K, 8.9 Torr 2-propanol, balance air, 40 cm^3 min^{-1} total flow.

selectivities are based on carbon content and are defined as the number of moles of 2-propanol reacted to each product per 100 moles of 2-propanol consumed. Table 2 shows a typical mass balance from the analyses at the inlet and outlet of the reactor, which all show 98.5+% closure. Acetone, propylene, carbon dioxide, and water with trace amounts (less than 0.05% carbon selectivity) of carbon monoxide were the only products observed. Although the reactor effluent was carefully analyzed for the presence of hydrogen, methane and isopropyl ether, these products were not observed when using air as the carrier gas. In all experiments using air as the reactant carrier, the molar amount of water detected in the exit stream was always equal to the sum of the molar amounts of propylene and acetone.

Data were also collected under differential conversion (0.1 to 0.8%) conditions at temperatures ranging from 448 to 598 K and used to estimate the product initial selectivities, listed as the selectivity at 0% conversion in Table 1. The product selectivities were observed to be only slightly dependent upon 2-propanol conversion, with selectivity to acetone minimally increasing with increasing conversion at the expense of propylene formation. These differential data were also used to determine initial reaction rates by plotting the fractional conversion versus the catalyst-to-flow ratio, with the slope of a line through the origin providing the initial rate (35), as illustrated in Fig. 1. Initial rates for 2-propanol consumption and product appearance are calculated from these data and presented in Table 1. The rate is presented as a turnover frequency (tof), in which the total number of active sites has been set equal to the number of sites active for the adsorption of 2-propanol determined from gravimetric and TPD experiments (6).

The initial rate data of Table 1 can also be plotted in Arrhenius form to provide a measure of the apparent activation energy of reaction and to more clearly illustrate the temperature dependence of the individual products, as shown in Fig. 2. The temperature dependence of the consumption of 2-propanol follows Arrhenius behavior with an apparent activation energy of 75 kJ/mol (Fig. 2a). The products, however, show differing activation energies, as expected by the temperature dependence of the product selectivities, with values ranging from 68 kJ/mol for acetone to 148 kJ/mol for carbon dioxide (Fig. 2b). The measured activation energy for propylene (130 kJ/mol) was significantly higher than that determined for acetone.

The initial rate of reaction and selectivity were determined in a similar fashion from differential conversion data collected at partial pressures of 2-propanol varying from 8.9 to 103 Torr at 548 and 598 K. The results, shown in Figs. 3 and 4, permit determination of the orders of the overall reaction and the individual product formation channels with respect to 2-propanol over the pressure range investigated. Although the observed order is slightly higher at 548 K (0.61) than at 598 K (0.52), the overall reaction appears to be approximately one-half order in 2-propanol at both 548 and 598 K. Similarly, the reaction orders of the products

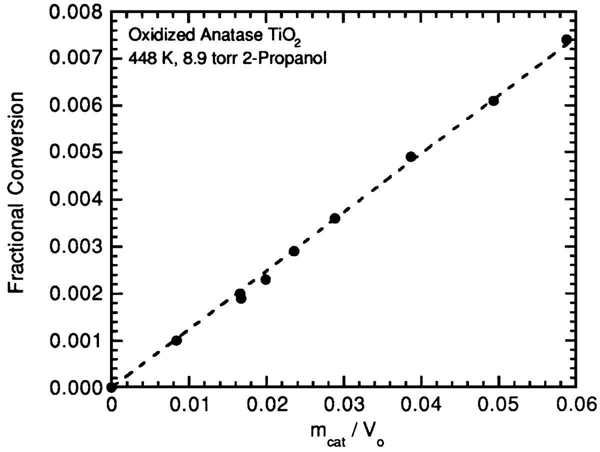


FIG. 1. Determination of initial rate of 2-propanol decomposition using dry air as the carrier gas. The fractional conversion of 2-propanol is plotted versus the ratio of the catalyst mass to the volumetric flow rate at constant temperature and inlet partial pressure of 2-propanol. The initial rate of reaction is given by the slope of a line passing though the data and the origin.

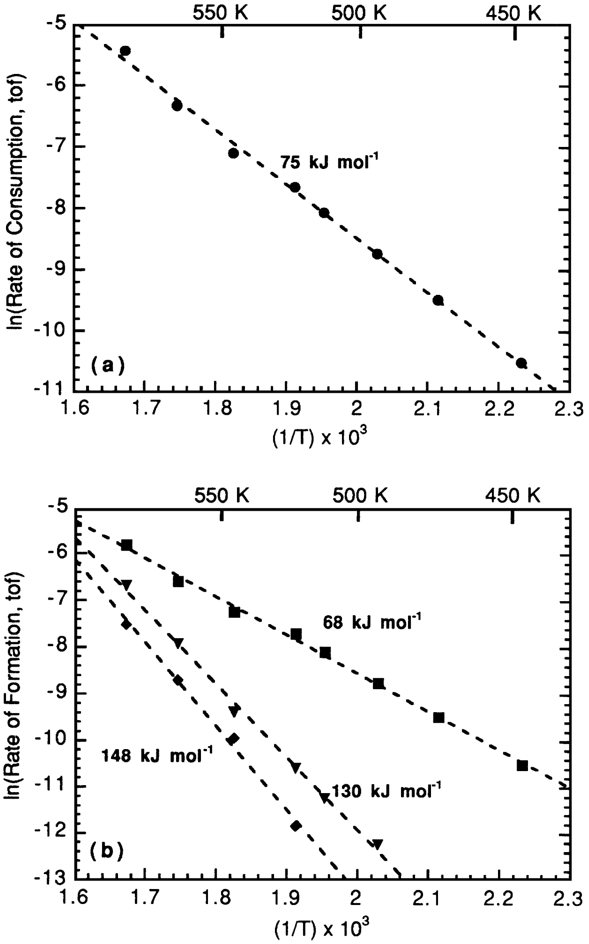


FIG. 2. Arrhenius plots for determining the apparent activation energy of the initial rate for (a) the consumption of 2-propanol and (b) the formation of dehydrogenation (acetone, ■), dehydration (propylene, ▼), and combustion (carbon dioxide, ◆) products. Temperature was varied between 448 and 598 K, and dry air was used as the carrier gas.

acetone and propylene are slightly higher at 548 K (0.63 and 0.48) than at 598 K (0.55 and 0.45) and approximately one-half order. The rate of formation of carbon dioxide, however, seems to shift from near zero-order at 548 K (0.15) to one-half order at 598 K (0.4).

As the small difference in reaction order suggests, there is a slight increase in selectivity to acetone formation at higher partial pressures of 2-propanol at both 548 and 598 K as indicated in Table 3. This increased selectivity is again only slightly dependent on 2-propanol conversion at higher partial pressures, which is also illustrated in Table 3. Again, the selectivity to acetone marginally increases with increasing 2-propanol conversion at the expense of propylene formation.

2. *Dry Helium as 2-Propanol Carrier*

The reaction of 2-propanol on oxidized titania using dry helium as carrier also produces dehydration and dehydrogenation products; however, the selectivity of the competing paths is now strongly dependent on both reaction temperature and conversion. Conversion and selectivity data collected between 548 and 598 K and at a 2-propanol partial pressure of 8.9 Torr are reported in Fig. 5. These data show selectivities for either acetone or propylene can range from 5 to 95% with inert carrier, depending on the reaction conditions. As expected, oxidation products such as carbon monoxide and carbon dioxide are not observed with an inert (helium) carrier gas. No products other than propylene, acetone, water and hydrogen were detected during experiments which yielded the data of Fig. 5. Under all conditions using an inert carrier gas, the detected amounts of dehydration products (water and propylene) were equivalent, as were the amounts of dehydrogenation products (hydrogen and acetone). A representative mass balance of reactor inlet and outlet streams is shown in Table 4; closure of all balances (total mass, C, H and O) was always greater than 98%.

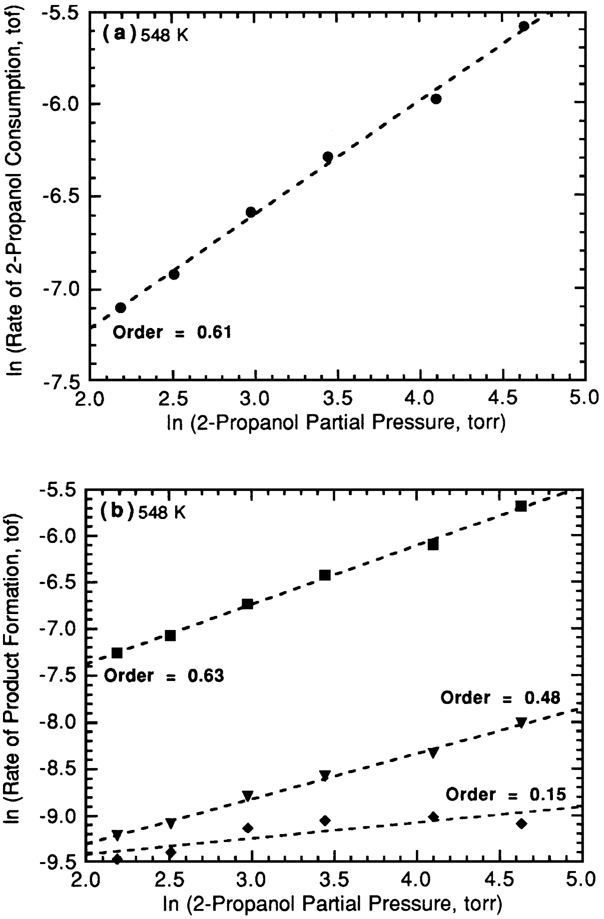


FIG. 3. Determination of the reaction order with respect to 2-propanol for (a) the overall consumption of 2-propanol and (b) the formation of the dehydrogenation (acetone, ■), dehydration (propylene, ▼), and combustion (carbon dioxide, ◆) products at 548 K. The partial pressure was varied between 8.9 and 120 Torr, and dry air was used as the carrier.

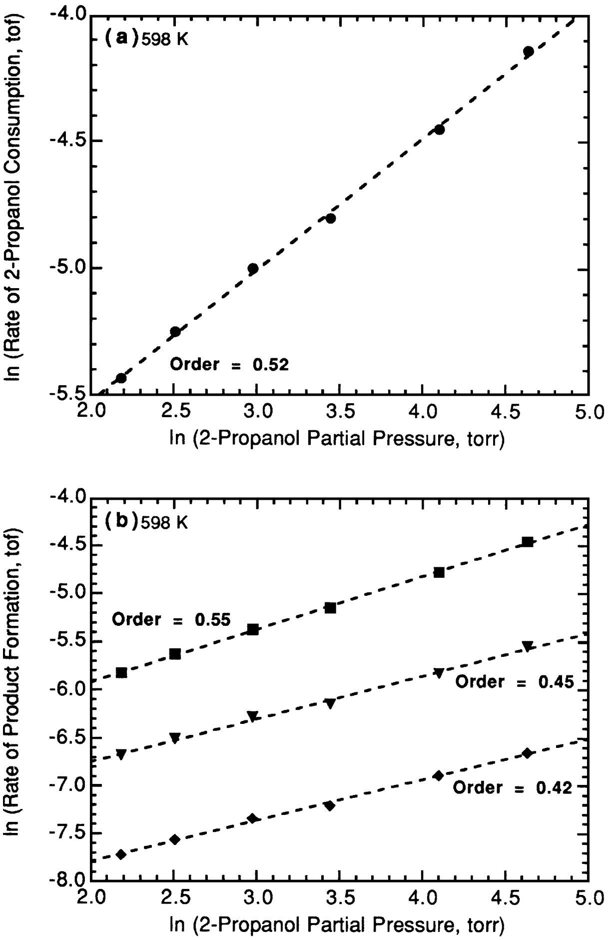


FIG. 4. Determination of the reaction order with respect to 2-propanol for (a) the overall consumption of 2-propanol and (b) the formation of the dehydrogenation (acetone, ■), dehydration (propylene, ▼), and combustion (carbon dioxide, ◆) products at 598 K. The partial pressure was varied between 8.9 and 120 Torr, and dry air was used as the carrier.

Because of the strong conversion dependence of the dehydration and dehydrogenation selectivities, initial rate determinations with dry helium carrier provide little insight. Instead, Table 5 reports the selectivities and formation rates of the dehydrogenation and dehydration products determined at representative conversions from 523 to 598 K at a 2-propanol partial pressure of 8.9 Torr. Also reported in Table 5 is the rate of consumption of 2-propanol at the indicated conversion.

An Arrhenius plot for 2-propanol consumption as a function of temperature constructed at a constant conversion (5%) is shown in Fig. 6. With increasing temperature, the apparent activation energy increases and a similar increase in the selectivity to propylene at constant conversion (see Fig. 5) is observed. This is consistent with the dehydration rate having a stronger temperature dependence than the dehydrogenation rate, as was observed in the air-carrier experiments. Indeed, the activation energy determined from Fig. 6 varies between 75 and 115 kJ/mol, depending upon which point (temperature) is chosen for calculation of the slope. The selectivity to acetone is highest in the region of low observed activation energy (i.e., low temperature, 75 kJ/mol), while propylene selectivity is greatest in the region of highest observed activation energy (i.e., high temperature, 115 kJ/mol). These values approach the values of 70 and 130 kJ/mol found for the dehydrogenation and dehydration rates, respectively, using air as the carrier.

TABLE 3

Dependence of 2-Propanol Decomposition Selectivity on Partial Pressure at 548 and 598 K on Oxidized Anatase TiO_2 with Air Carrier

Temp. (K)	Pressure (Torr)	Conv. (%)	Selectivity C_3H_6	Selectivity CO_2	Selectivity $(CH_3)_2CO$
548	8.9	0	12.1	3.0	84.9
		1.75	11.9	3.1	85.0
	31.3	0	11.6	2.5	85.9
		1.98	9.1	2.5	88.4
	102.7	0	10.0	1.1	88.9
		2.21	6.0	1.0	93.0
598	8.9	0	29.3	3.1	67.6
		6.89	26.4	4.9	68.7
	31.3	0	27.9	2.9	69.2
		7.53	26.8	4.4	68.8
	102.7	0	24.6	2.7	72.8
		8.21	24.0	4.0	72.0

Increasing the partial pressure of 2-propanol increases the dehydrogenation selectivity at constant conversion at the expense of the dehydration products. Figure 7 shows the dependence of the dehydrogenation and dehydration selectivities on 2-propanol partial pressure and conversion at 548 K and a partial pressure range of 8.9 to 120.7 Torr. A similar trend was observed using air as the carrier: the dehydrogenation selectivity increased with increasing partial

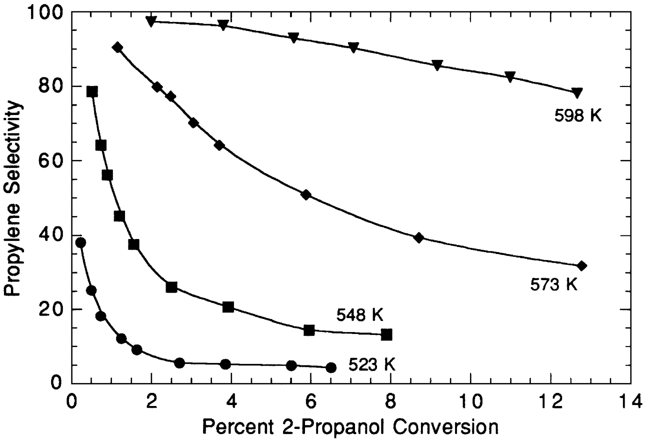


FIG. 5. Conversion dependence of the 2-propanol decomposition selectivity as a function of reaction temperature at 8.9 Torr 2-propanol using helium as the carrier gas.

TABLE 4

Typical Mass and Atom Balance for 2-Propanol Decomposition Reaction on Anatase TiO_2 Using Helium as the Carrier

	Inlet	Outlet				
	$(CH_3)_2CHOH$	$(CH_3)_2CHOH$	H_2	H_2O	$(CH_3)_2CO$	C_3H_6
	1.149	1.003	0.0007	0.0340	0.0307	0.0799
C	0.6894	C	0.6893			
H	0.1532	H	0.1528			
O	0.3064	O	0.3062			
Total	1.1490	Total	1.1483			

Note. All values are mg per minute. Conditions: 548 K, 8.9 Torr 2-propanol, balance helium, 40 $cm^3\ min^{-1}$ total flow.

pressure of 2-propanol (see Table 3). Identical behavior was observed at all temperatures investigated, though the dehydration rate was much less dependent on partial pressure than on temperature. Accordingly, only small selectivity changes were observed with increasing partial pressure at higher temperatures.

At the combination of the highest partial pressure (120.7 Torr) and the highest temperature (598 K) investigated, isopropyl ether was observed as a product when using helium as carrier with a selectivity ranging from 4.0 to 1.4%, decreasing with increasing conversion. These data are indicated at the bottom of Table 5. Isopropyl ether was not observed under any other conditions, nor was isopropyl ether observed under the identical conditions when air was used as carrier.

3. *Wet Helium as 2-Propanol Carrier*

Early in the investigation it was recognized that the amount of water vapor in the reactor could play an important role in directing the 2-propanol decomposition selectivity. Since decomposition in air carrier results in both a higher dehydrogenation selectivity and a larger amount of water than reaction in helium carrier, it was hypothesized that enhanced dehydrogenation selectivities may result from increased levels of water. Such an effect of water could also be responsible for the increase in dehydrogenation

TABLE 5

Conversion, Selectivity, and Rate of Reactant Consumption and Product Formation for 2-Propanol Decomposition on Oxidized Anatase TiO_2 at a Partial Pressure of 8.9 Torr, Using Helium as the Carrier

Temp. (K)	Conv. (%)	Selectivity			Rate of formation (s^{-1})			Rate of consumption (s^{-1})
		C_3H_6	IPE[a]	$(CH_3)_2CO$	C_3H_6	IPE[a]	$(CH_3)_2CO$	$(CH_3)_2CHOH$
523	0.23	38.1		61.9	2.47×10^{-5}		4.01×10^{-5}	6.48×10^{-5}
	0.73	18.2		81.8	2.33×10^{-5}		1.05×10^{-4}	1.28×10^{-4}
	1.63	9.2		90.8	2.01×10^{-5}		1.99×10^{-4}	2.19×10^{-4}
	3.85	5.3		94.7	1.93×10^{-5}		3.45×10^{-4}	3.64×10^{-4}
548	0.53	78.6		21.4	9.59×10^{-5}		2.61×10^{-5}	1.22×10^{-4}
	0.91	56.2		43.8	8.65×10^{-5}		6.75×10^{-5}	1.54×10^{-4}
	1.56	37.6		62.4	7.97×10^{-5}		1.32×10^{-4}	2.12×10^{-4}
	3.92	20.7		79.3	7.68×10^{-5}		2.94×10^{-4}	3.71×10^{-4}
573	2.15	79.8		20.2	3.93×10^{-4}		9.94×10^{-5}	4.92×10^{-4}
	2.49	77.3		22.7	3.43×10^{-4}		1.01×10^{-4}	4.44×10^{-4}
	3.71	64.2		35.8	3.23×10^{-4}		1.80×10^{-4}	5.03×10^{-4}
	5.88	50.9		49.1	2.79×10^{-4}		2.69×10^{-4}	5.48×10^{-4}
598	5.57	92.9		7.1	1.20×10^{-3}		9.16×10^{-5}	1.29×10^{-3}
	7.07	90.3		9.7	1.15×10^{-3}		1.23×10^{-4}	1.27×10^{-3}
	9.17	85.5		14.5	1.07×10^{-3}		1.81×10^{-4}	1.25×10^{-3}
	12.67	78.1		21.9	9.37×10^{-4}		2.63×10^{-4}	1.20×10^{-3}
548[b]	0.13	73.7		26.3	2.59×10^{-4}		9.23×10^{-5}	3.51×10^{-4}
	0.16	69.1		30.9	2.26×10^{-4}		1.01×10^{-4}	3.28×10^{-4}
	0.26	56.8		43.2	2.17×10^{-4}		1.65×10^{-4}	3.82×10^{-4}
	0.42	47.6		52.4	1.99×10^{-4}		2.19×10^{-4}	4.18×10^{-4}
598[b]	1.98	84.9	3.8	11.3	4.49×10^{-3}	9.94×10^{-5}	5.98×10^{-4}	5.19×10^{-3}
	2.49	85.7	2.9	11.4	4.26×10^{-3}	7.27×10^{-5}	5.65×10^{-4}	4.90×10^{-3}
	3.08	85.0	2.5	12.5	4.13×10^{-3}	6.31×10^{-5}	6.05×10^{-4}	4.80×10^{-3}
	4.12	84.5	1.4	14.1	3.72×10^{-3}	3.05×10^{-5}	6.24×10^{-4}	4.37×10^{-3}

Note. Turnover frequency (tof) calculated based upon 2-propanol saturation coverage of 2.22 molecules per nm^2 (6).

[a] IPE: isopropyl ether.

[b] 2-propanol partial pressure of 120.7 Torr.

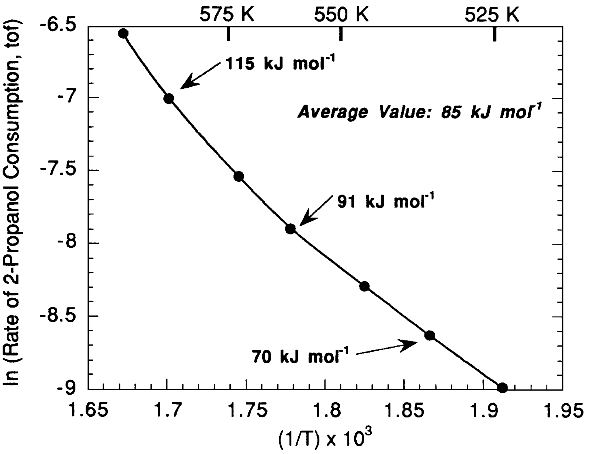


FIG. 6. Arrhenius plot for determining the apparent activation energy for 2-propanol decomposition at a constant conversion of 5%. The activation energy varies between 70 and 131 kJ mol^{-1} in the temperature range investigated (523 to 598 K) with helium as the carrier gas. Over the entire range, the average apparent activation energy is 85 kJ mol^{-1}.

selectivity which is observed with increasing conversion. Therefore, to investigate the role of water in the dependence of 2-propanol decomposition selectivity on conversion, varying amounts of water were added to the dry helium carrier gas used in the experiments. This was accomplished by simply mixing 2-propanol with water in varying amounts and placing this mixture into the saturator. The temperature of the saturator was then adjusted to provide the proper partial pressure of 2-propanol, as measured by the on-line gas chromatograph using the thermal conductivity detector. The amount of water in the feed was then also determined by this same method; the ratio of water to 2-propanol could be conveniently altered and carefully monitored by this simple procedure.

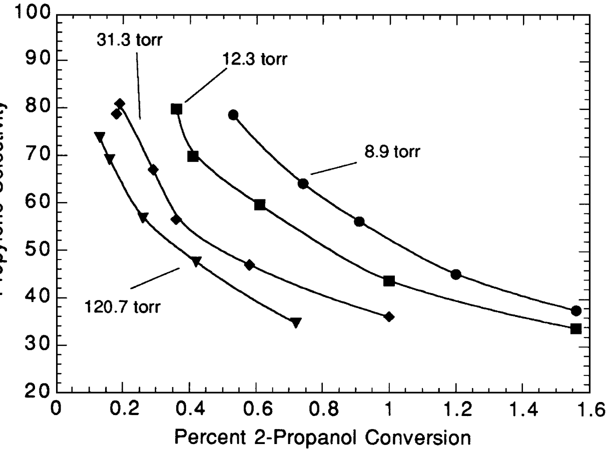


FIG. 7. Conversion dependence of the 2-propanol decomposition selectivity to propylene as a function of 2-propanol partial pressure at 548 K using helium as the carrier gas. At 548 K, acetone is the only other carbon-containing product formed; consequently, acetone selectivity is simply 100 minus the selectivity to propylene.

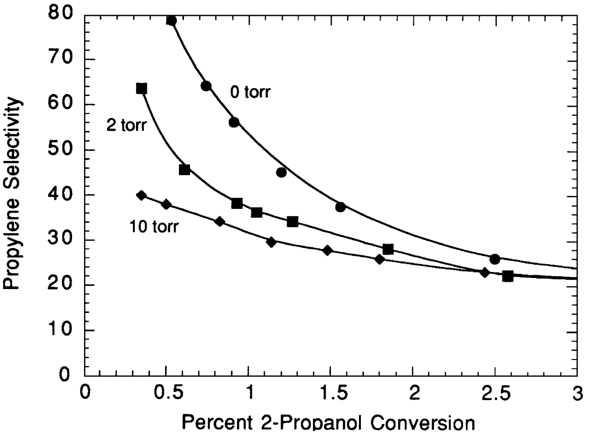


FIG. 8. Conversion dependence of the 2-propanol decomposition selectivity to propylene as a function of the partial pressure of added water at 548 K using helium as the carrier gas. The partial pressure of 2-propanol in the feed stream was held constant at 8.9 Torr. Acetone is the only other carbon-containing product formed; consequently, acetone selectivity is simply 100 minus the selectivity to propylene.

Addition of relatively small amounts of water produces a profound effect on the selectivity of the 2-propanol decomposition pathways at constant conversion. Figure 8 shows that the dehydration selectivity of 2-propanol decreases at constant conversion as additional water is fed to the reactor at 548 K. The observed effect is strong enough to completely invert the product selectivities at 1% conversion or less upon the addition of 10 Torr of water. The effect observed is caused by some phenomenon other than a shift in reaction equilibrium, as the maximum conversion in these experiments (5%) is still well removed from the theoretical 2-propanol equilibrium conversion of 98% at the reaction conditions employed. Most interesting is the weakened conversion dependence of the 2-propanol decomposition selectivity with increasing water content for the range of conversions investigated. Analysis of the product rates of formation at 0.5% 2-propanol conversion, shown in Table 6, indicates the selectivity shift with increasing water content is due to an increased rate of acetone formation; propylene continues to be produced at a nearly constant rate. This suggests that the presence of water or an adsorbed form of water may aid in the formation of acetone from 2-propanol on oxidized anatase TiO_2.

4. Oxygen in Dry Helium as 2-Propanol Carrier

The disparate nature of the effect of conversion on selectivity for the decomposition pathways of 2-propanol when using dry helium or dry air as carrier gas was further investigated. By mixing dry oxygen and dry helium together in varying amounts, the oxygen content of the carrier could be precisely controlled, measured using a gas chromatograph with a thermal conductivity detector, and utilized as

TABLE 6

Conversion, Selectivity, and Rate of Reactant Consumption and Product Formation for 2-Propanol Decomposition at 548 K on Oxidized Anatase TiO_2 at a Partial Pressure of 8.9 Torr, Using Helium as the Carrier with Added Water

P_{Water} (Torr)	Conv. (%)	Selectivity C_3H_6	Selectivity $(CH_3)_2CO$	Rate of formation (s^{-1}) C_3H_6	Rate of formation (s^{-1}) $(CH_3)_2CO$	Rate of consumption (s^{-1}) $(CH_3)_2CHOH$
0	0.53	78.6	21.4	9.59×10^{-5}	2.61×10^{-5}	1.22×10^{-4}
2.0	0.61	45.7	54.3	9.48×10^{-5}	1.13×10^{-4}	2.07×10^{-4}
10.0	0.47	37.9	62.1	9.45×10^{-5}	1.55×10^{-4}	2.49×10^{-4}

Note. Turnover frequency (tof) calculated based upon 2-propanol saturation coverage of 2.22 molecules per nm^2 (6).

a carrier gas in the decomposition of 2-propanol over oxidized anatase titanium dioxide.

The partial pressure of oxygen in the carrier gas was varied from 0 to 20%, while the partial pressure of 2-propanol (8.9 Torr) and the conversion (1%) were held constant, and the selectivity of the dehydrogenation and dehydration paths for 2-propanol were monitored at 548 K. The results, shown in Fig. 9a, indicate that the selectivity shifts dramatically from the dominance of a dehydration path in an oxygen-free carrier to dehydrogenation dominance in an oxygen-rich environment at a constant, low (1%) conversion. Further, this shift is due to a dramatic increase in the rate of acetone formation with increasing carrier oxygen content, while the rate of propylene formation is independent of the amount of oxygen in the carrier gas as shown in Fig. 9b. As was the case when air was used as reactant carrier, the addition of even the smallest amount of oxygen results in the complete elimination of hydrogen formation; the molar amount of water observed in the effluent was equivalent to the sum of the molar amounts of acetone and propylene.

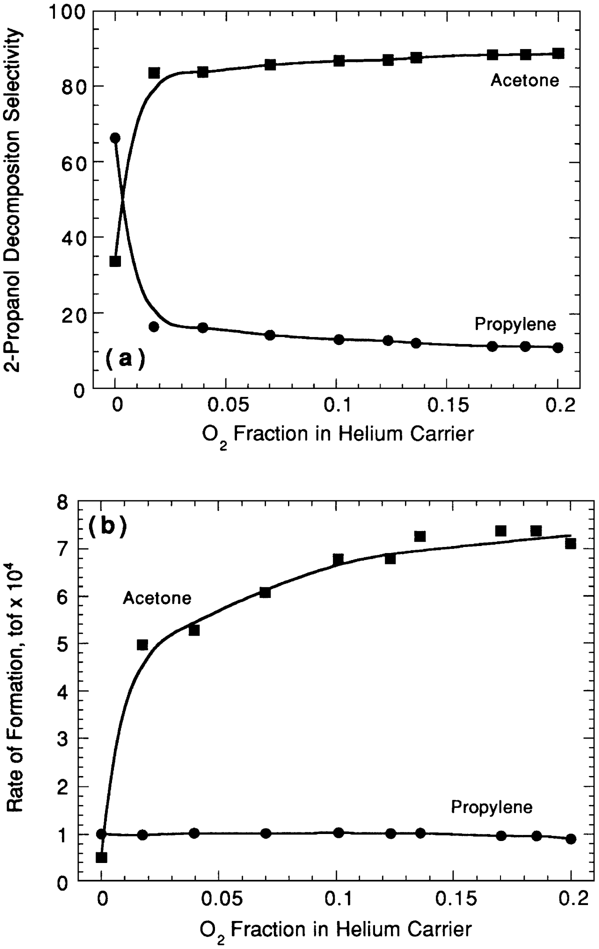


FIG. 9. Dependence of 2-propanol decomposition selectivity (a) and product rates (b) as a function of oxygen incorporated into dry helium carrier gas at 548 K. 2-propanol partial pressure is 8.9 Torr, and conversion is constant at 1(±0.05)%.

DISCUSSION

1. *General Observations and Comparisons*

The characterization of surface acid–base properties by 2-propanol decomposition is typically carried out between 450 and 550 K with approximately 1–3% alcohol in a large excess of air (8, 27). The results presented above indicate the need for caution when interpreting dehydration and dehydrogenation selectivities from 2-propanol decomposition under these typical conditions in terms of surface acid and base properties of metal oxides. The dehydrogenation selectivity can vary substantially with reaction temperature, from nearly 100% at 473 K and below to 68% at 598 K, as indicated in Table 1. Less dramatic, but nonetheless important, partial pressure and conversion have also been demonstrated to impact the relative rates of the dehydration and dehydrogenation pathways (see Tables 1 and 3). Further, as illustrated by the wide range of rates and selectivities obtained, the choice of inert or oxidizing carrier gas has a profound effect not only on the reaction selectivity but also on the underlying kinetics of the decomposition process. Consequently, the interpretation of selectivity or rate data from one catalyst to another in terms of acid–base properties can be substantially complicated by the conditions chosen to perform the characterization.

The observation of high selectivity to acetone for 2-propanol decomposition on TiO_2 is consistent with several previous observations. Bond and Flamerz (9) reported an initial selectivity to dehydrogenation of 66% at 475 K using an unwashed sample of anatase TiO_2 with helium as the carrier gas. Cunningham and co-workers (34) observed a 96% selectivity to acetone formation at 475 K on a high surface area titania in steady state experiments using a combination of N_2 and O_2 as a carrier. Grzybowska-Swierkosz (10) reported a 71% selectivity to acetone in pulse experiments with inert N_2 as the carrier at 443 K. Cunningham and Hodnett (36) studied the photoassisted decomposition of 2-propanol on TiO_2 at low temperature (348 K) and found nearly 100% selectivity toward the dehydrogenation route in the presence of oxygen. These experiments, including the results reported here, were all performed with TiO_2 samples prepared either by chloride or alkoxide processes (37). These results contrast with those of Gervasini and Auroux (8), who observed low selectivity to acetone formation on TiO_2 using air as the carrier at 450 K. The sample of TiO_2 used by Gervasini and Auroux was reported to contain 1% SO_4 (17), leading to the relatively high acidity reported for this material (8, 17).

The kinetics determined in the present study are also consistent with several previously reported kinetic parameters for 2-propanol decomposition on TiO_2; however, significant variations in experimental results for the dehydrogenation pathway are noted. In general, the rate of acetone formation in the present study is larger than reported in previous studies. Even here, however, substantial ambiguity is present. Cunningham *et al.* (34), for example, report rates for acetone formation which, when converted to a turnover frequency (tof) using the adsorption density of 2-propanol on TiO_2 (6), range from 1.8×10^{-5} to 1.5×10^{-3} s^{-1} for different samples of TiO_2 at 475 K using an N_2/O_2 carrier gas mixture. Gervasini and Auroux (8) report a rate, converted to a tof as described above, of 1.2×10^{-7} s^{-1} for acetone formation at 475 K in an air carrier. These values bracket our observed turnover frequency of 7.7×10^{-5} s^{-1} at 473 K using air as the carrier. Bond and Flamerz report a rate of acetone formation corresponding to a tof value of 1.5×10^{-3} s^{-1} on an unwashed sample of a low surface area (9.6 m^2/g) commercial (Tioxide) TiO_2 using an inert carrier gas (N_2) at 475 K. This is significantly larger than our estimated value of 7.3×10^{-5} s^{-1} at 4% conversion, which was obtained by extrapolation of our results with an inert carrier to the same conditions of Bond and Flamerz. It must be stressed, however, that Bond and Flamerz report only that conversions were typically below 15% in their experiments; our results would indicate the acetone rate and selectivity will increase dramatically with increasing conversion at these conditions. This is illustrated in Table 5, where the tof for acetone formation at 523 K varies from 6.5×10^{-5} to 3.6×10^{-4} s^{-1} as the conversion is increased from 0.2 to 3.9%.

Better agreement is observed when comparing the rate of propylene formation. Cunningham and co-workers (34) report rates which, when converted to tof, have values from 6.3×10^{-6} to 5.2×10^{-5} s^{-1} at 475 K in an N_2/O_2 carrier, again depending on the source of TiO_2. Gervasini and Auroux (8) report a rate with tof values of 1.8×10^{-6} s^{-1} for propylene formation at 475 K in an air carrier. These values are quite similar to our tof for propylene of 1.1×10^{-6} s^{-1} measured at 473 K in air carrier. Bond and Flamerz (9) report rates of propylene formation for three different TiO_2 samples which correspond to tof values ranging from 7.8×10^{-5} to 8.2×10^{-4} s^{-1} using pure N_2 as the carrier at 475 K. These rates are only slightly higher than values at the identical conditions which can be estimated from our results presented in Table 5. Comparison of the results of Cunningham *et al.* (34) and Gervasini and Auroux (8) (oxidizing carrier gases) with those of Bond and Flamerz (9) (inert carrier), as well as the results of the present study, clearly indicate the difference in the carrier gas composition is likely responsible for the apparent inconsistencies noted here.

The activation energy for the dehydrogenation pathway was determined in the present study to be 70 kJ mol^{-1}. This value is similar to values previously reported when using an oxidizing carrier gas, which range from 63 to 109 kJ mol^{-1} (8, 9, 34) depending on the method of determination and TiO_2 source. Similar to the rate observations, literature values for the activation energy for dehydration of 2-propanol on TiO_2 are less varied, ranging from 126 to 149 kJ mol^{-1} (8, 9, 34). These compare quite favorably to the present results, in which the activation energy for dehydration was determined to be 130 kJ mol^{-1}.

The overall decomposition of 2-propanol on TiO_2 was determined to be one-half order with respect to the reactant partial pressure in an air carrier. This contrasts to the usual assumption of zero-order kinetics in alcohol decomposition on metal oxides (8, 24). This assumption, however, appears to be based upon a crude determination of reaction order for 2-propanol decomposition on a MoO_3–P_2O_5 catalyst (32). The reaction order was also determined by Kochloefl and Knözinger (12) for 2-propanol decomposition on several metal oxides, including TiO_2, in an inert carrier gas, by varying the partial pressure within the range of 100 to 700 Torr. These authors found the dependence upon the partial pressure of 2-propanol to be a complex function, with positive order at low partial pressures and zero or negative order kinetics at high partial pressures. The range of pressures used by Kochloefl and Knözinger is considerably higher than in the present study, in which the order was determined by varying the partial pressure between 8.9 and 120.7 Torr; values ranging from 5 to 100 Torr are more commonly used in 2-propanol decomposition studies on metal oxides (8, 9, 24, 34). It is likely, however, that if sufficiently high partial pressures are employed, surface saturation will occur and the reaction would approach zero order.

The kinetics results are also consistent with results from this laboratory (6, 20, 21) and others (3, 4, 38) employing TPD methods. When using helium as carrier gas, the dehydration of 2-propanol dominates in both the TPD and steady-state experiments. However, when a mixture of 20% O_2 in inert is used as carrier, the amount of acetone formed is increased and the quantity of propylene is simultaneously decreased (38), consistent with the observed selectivity shift in the steady-state experiments. The desorption peak for propylene is observed to be preceded slightly in temperature by the desorption of acetone (555 K for acetone to 570 K for propylene (6)). This is qualitatively consistent with the lower observed activation energy for dehydrogenation than dehydration found in steady state experiments using both helium and air as carriers.

The magnitude of the activation energy difference for dehydration and dehydrogenation estimated from TPD experiments (6–8 kJ mol^{-1}) is smaller than suggested by the steady-state experiments, though estimation in the latter case is complicated by the strong conversion dependence of the dehydrogenation reaction rate. This apparent discrepancy may be related to method of kinetic measurement and the demonstrated complications created by the presence of water vapor (see Fig. 8 and discussion below), a product of the dehydration reaction. Further, the TPD measurement effectively probes reaction kinetics at very low conversions, as low concentration vapor- and surface-phase products are present during a typical TPD experiment, as well as at low reaction rates, since each site is responsible for essentially one turnover. Conversely, the steady-state experiments are performed at conversions (ca. 5%), which provide non-negligible amounts of products in both the vapor and the adsorbed state, as well as requiring multiple turnovers at each reactive site. Therefore, any effect of water, for example, would likely be absent in TPD experiments but present in steady-state experiments, resulting in apparently inconsistent kinetic observations. We discuss possibilities for the role of water in the decomposition of 2-propanol on oxidized TiO_2 powders in the following section.

Analysis of the leading-edge of the thermal desorption spectra of acetone and propylene from 2-propanol decomposition on TiO_2 of Lusvardi *et al.* (6) and Larson *et al.* (38) provides another interesting comparison to the steady-state reaction results presented above. The acetone desorption traces reported by both groups show very asymmetric shapes, with desorption rates for acetone being larger than propylene at temperatures on the leading-edge of the acetone desorption feature. Quantitative comparison of the leading-edges of these peaks provides an estimated 2 : 1 ratio of the formation rate of acetone to propylene at 525 K. This value should be similar to the steady-state reaction selectivity ratio below about 525 K at low conversion. Indeed, this correspondence is observed, as the selectivity ratio at steady-state was observed to be 1.7 : 1 at 523 K (see Table 5).

Aside from dehydration and dehydrogenation products, total oxidation products and isopropyl ether were also observed in very small quantities. Total oxidation products were observed only in the presence of excess O_2, consistent with the known poor oxidation activity of TiO_2 (39–41). Isopropyl ether formation was only formed in inert carrier gas streams; under otherwise identical conditions, reactions with inert carrier gas would produce small amounts of isopropyl ether while reactions in an oxidizing carrier would not. Further, the formation of isopropyl ether was observed only at high partial pressures of 2-propanol, indicating a reaction order for ether formation from 2-propanol higher than those for dehydration and dehydrogenation.

Bimolecular reactions of alcohols to form ethers on TiO_2 have been shown to require doubly coordinatively unsaturated surface cations (20) in order to allow coupling of adsorbed alkoxide species. Such sites have been shown to exist on the surface of anatase and rutile TiO_2 powders (6) giving rise to the formation of ethers from methanol and ethanol in temperature-programmed desorption experiments on these materials. However, the absence of isopropyl ether formation at low partial pressures is not unexpected because of the larger steric hindrance associated with branched alkoxides. The higher surface coverages associated with higher partial pressures of 2-propanol require alkoxide species to overcome this steric inhibition toward attachment of two alkoxides at a common cation, and bimolecular reactions can begin to occur. The presence of an oxidizing environment results in the formation of larger quantities of water. While alcohols can effectively compete with water for adsorption sites on TiO_2, the presence of water may add to the steric hindrance, shifting the onset of attachment of the second alkoxide ligand to a single Ti cation to even higher partial pressures. This suggestion is consistent with the results of Lusvardi *et al.* (42) who showed that the concentration of ethoxide species formed from ethanol adsorption on oxidized TiO_2 decreases with preadsorption of water. Also, Gamble *et al.* (43) demonstrated that water plays a significant role in the high-temperature (>500 K) reaction chemistry of ethanol adsorbed on an oxidized $TiO_2(110)$ single crystal. As a result, conditions which permit the onset of bimolecular reactions in an inert atmosphere may be insufficient for such reactions in an oxidizing carrier or when sufficient concentrations of water vapor are present.

2. *The Oxidative Role of Oxygen and Water*

It has been suggested (8) that utilizing air as the carrier gas in 2-propanol decomposition studies on reducible metal oxides is essential to avoid surface reduction, and thus alteration of selectivities during the course of the characterization reaction. While the tendency for alcohols to undergo deoxygenation reactions on reduced metal oxide surfaces has been demonstrated (20) and would be consistent with the higher dehydration selectivity observed using an inert carrier, TiO_2 surface reduction seems unlikely under the relatively mild conditions of alcohol decomposition. Indeed, the present results underscore the improbability of surface reduction during alcohol decomposition. Propylene, the dominant product of 2-propanol reaction with reduced TiO_2 surfaces, is formed at identical rates regardless of the use of air or helium as the carrier gas (see Tables 1 and 5 and Fig. 9). Further, surface reduction by 2-propanol would be accompanied by formation of water and perhaps carbon oxides or surface carbon deposition. In helium carrier experiments, the amount of water detected always equaled the molar amount of propylene formed, and no carbon oxides were detected. Deposition of surface carbon would likely result in a diminution of the reaction rate over time; however, the catalysts were tested and found stable at all conditions for on-stream times in excess of 40 h. On the basis of these results, the role of oxygen in the decomposition pathways of 2-propanol on TiO_2 cannot be ascribed solely to the elimination of surface reduction.

The lack of hydrogen production and the equivalence of the molar amount of water produced to the sum of acetone and propylene suggests the dehydrogenation of 2-propanol in the presence of O_2 proceeds via an oxidative route. This conclusion is also supported by the experiments in which O_2 was added in varying amounts to dry helium and fed to the reactor. As illustrated in Fig. 9, the addition of even small amounts of O_2 to helium results in a dramatic shift in the selectivity, from the dominance of the dehydration path in the absence of air to 85+% selectivity to the dehydrogenation product with the addition of 10 Torr of O_2. Even more striking is the independence of the rate of propylene formation on the amount of O_2 in the carrier gas while the formation of acetone increases by an order of magnitude with the addition of 10 Torr of O_2. All of these features point to the opening of a new, more rapid pathway for the formation of acetone in the presence of O_2, with oxidative dehydrogenation providing a plausible explanation.

As Table 5 indicates, high selectivities to acetone can be achieved without the presence of O_2 in the carrier gas when the conversion is appropriately high. However, a comparison of the results in Tables 1 and 5 indicates that superior acetone yields are obtained with air as carrier, regardless of conversion. Interestingly, the changes in selectivity with increasing conversion of 2-propanol seem to slow and eventually plateau at sufficiently high conversions. The position of this selectivity plateau, at least for operation at 523 and 548 K where it is clearly defined, is nearly identical to the selectivity obtained when using air as the carrier gas. Further, the rates observed at higher conversion in Table 5 approach the values obtained when using air as a carrier gas.

As water is generated in increasing amounts with increasing 2-propanol conversion, the *in situ* formation of water through the dehydration of 2-propanol may explain the increase in acetone selectivity and rate with increasing conversion of 2-propanol in an inert carrier. As more water is produced via the dehydration route, more water is present in the reactor and the selectivity to acetone increases. With the addition of water to the helium carrier gas, a shift to higher dehydrogenation selectivity is observed, as shown in Fig. 8. More importantly, the selectivity becomes much less strongly dependent upon the conversion of 2-propanol at low conversions, while the selectivity at higher conversions still plateaus at the same value regardless of the amount of water added. The value of this selectivity plateau at high conversion is also identical to that observed when no additional water is fed to the reactor, as indicated in Fig. 8. In effect, the presence of added water expands the range of 2-propanol conversion in which the selectivity is independent of reaction extent; the addition of more water shifts the onset of this relative independence to lower conversions. When using air as the carrier, the water concentration is higher than when using an inert carrier when compared at identical conversions, because water is formed from both dehydration and dehydrogenation routes. As a result, the effects of increasing conversion are diminished when using air as carrier.

The addition of 10 Torr water to the inert carrier also results in an increased rate of dehydrogenation by an order of magnitude, while leaving the rate of dehydration unchanged (see Table 6). This is the opposite to the effect expected if the dehydration equilibrium were shifted by the addition of water: the apparent dehydration rate should decrease, leaving the dehydrogenation rate unaffected. A kinetic effect, rather than a thermodynamic one, is thus indicated by the rate data. The oxidation of propylene to form acetone has been reported on mixed metal oxides under reaction conditions similar to those employed here (44) and would be consistent with many of the experimental observations. However, at temperatures and pressures consistent with those of the 2-propanol decomposition results, propylene and water do not react to any measurable degree over TiO_2.

In many respects, the role of water as observed in the present results, both added and generated by reaction, is similar to the oxidative role of O_2 in the decomposition of 2-propanol on oxidized TiO_2. The presence of O_2, of added water or of substantial amounts of water from high conversions of 2-propanol all dramatically increase the rate of acetone formation from 2-propanol on oxidized anatase TiO_2 while leaving the propylene rate essentially unchanged. Further, the observed rates of product formation are quite similar in the presence of O_2, added water, or water generated through dehydration at high conversion, resulting in very similar product distributions under these conditions. Therefore, it seems likely that the effect of added O_2 does not result from the direct interaction of O_2 with the reactants or products, but from the increased amounts of water created during the course of reaction with O_2 present. Either way, these results suggest the presence of water (or a derivative of water, i.e., hydroxyl groups) and/or the presence of O_2 opens a new or enhances an existing route for the formation of acetone from 2-propanol.

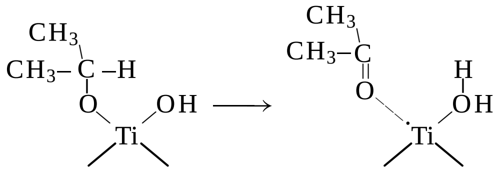
Several examples of hydroxyl-assisted reaction pathways on metal oxides can be found in the literature. Chadwick and Zheng (45) reported a significant influence of adsorbed water and hydroxyls on methanol decomposition pathways on ZnO during temperature-programmed desorption experiments. The authors observed that the decomposition of methanol on dehydroxylated ZnO results in the formation of CO and H_2. When water was coadsorbed, the product slate included CO_2; as the preadsorbed water was increased, the amount of CO formed decreased linearly, while the amount of CO_2 increased. The authors suggested that this changing product spectrum represents the opening of a new reaction channel to CO_2 formation as the surface hydroxyl concentration increases, probably through a direct reaction between adsorbed methoxy or a related intermediate and surface OH groups. Shido and Iwasawa (46) have similarly proposed a reactant-promoted reaction mechanism for the water–gas shift reaction over ZnO in which adsorbed CO reacts with surface hydroxyl groups to produce intermediate formate species. Both of these studies illustrate the potentially important role that surface hydroxyl groups and/or water may play in reactions on metal oxides.

The increase caused by the external addition of water, however, is not as pronounced as the increase caused by even smaller amounts of water generated *in situ* from the dehydration pathway or when the reaction is carried out in the presence of O_2. The partial pressure of water generated *in situ* from dehydration is typically less than 0.5 Torr, as calculated from the reaction mass balances, compared to 2–10 Torr in the addition experiments. These observations can be easily reconciled if one assumes the species active for enhanced dehydrogenation are hydroxyl groups rather than adsorbed water. The direct synthesis of hydroxyl groups from alcohol dehydration (or formed under oxidative conditions) would likely occur more rapidly than the dissociation of water adsorbed from the gas phase, especially considering the known inhibition of water adsorption by adsorbed alcohols and alkoxides (42, 43). As a result, a larger concentration of externally added water would be required in the gas phase to achieve the same surface hydroxyl concentration (and the corresponding dehydrogenation rate increase) that occurs from *in situ* generation.

3. *Comments on the Mechanism of 2-Propanol Decomposition*

The decomposition of 2-propanol has been extensively utilized as a probe reaction for determining the acid–base properties of metal oxides. It has often been asserted that dehydrogenation occurs as a concerted process on both acidic and basic sites, while dehydration occurs predominantly on acidic sites (27, 33). Regardless of the nature of the active site or sites, the present results indicate the rate of dehydration is stable and independent of the conversion and the carrier gas composition. Thus, it appears there is some fraction of the adsorbed species which readily dehydrates. While the rate of the dehydration route is dependent upon temperature and 2-propanol pressure, the rate is independent of the carrier gas composition and water content.

In contrast, the presence or absence of water or hydroxyl groups dramatically enhances the dehydrogenation selectivity of 2-propanol decomposition on TiO_2. We propose that this enhancement occurs through an α-H abstraction step involving an alkoxide and a hydoxyl group bound to the same Ti cation:



The existence of a hydroxyl-mediated dehydrogenation step would consolidate many of the present experimental observations. Such a step would be consistent with the observed dehydrogenation selectivity increase with increasing water concentration in an inert carrier. Additionally, the conversion dependence of the decomposition selectivity can be explained: larger quantities of *in situ* water and hydroxyls are present at higher conversions, resulting in the generation of additional species responsible for dehydrogenation. The kinetics of the dehydrogenation and dehydration reactions determined at steady state are considerably different. The order with respect to 2-propanol, while near one-half in both cases, is always higher for dehydrogenation, and the activation energies are nearly a factor of two different. These observations alone suggest the decomposition of 2-propoxide toward dehydration and dehydrogenation products must involve different active sites and/or different intermediates.

As both alkoxides and hydroxyls are present on the same cation in the proposed scheme, increasing the partial pressure of 2-propanol may result in increased hydoxyl populations from dissociation of the alcohol, further enhancing the rate of dehydrogenation. This trend is observed using both air and inert carrier gases (see Tables 3 and 5 and Fig. 7). One might argue that increased 2-propanol partial pressure could also lead to lower concentrations of surface hydroxyls from site competition. While this may in fact may reduce the *total* hydroxyl coverage of the surface, only hydroxyls bound with alkoxides to a common Ti cation are proposed to be active for dehydrogenation. If alcohols could displace these hydroxyls, two alkoxides would be bound to a common Ti cation, resulting in bimolecular reactions such as ether formation (6, 20, 21, 47). In the present study, isopropyl ether was only formed in inert carrier at the combination of the highest temperature and highest partial pressure of 2-propanol investigated; further, the selectivity to isopropyl ether never exceeded 4%. Based on the reaction products observed, the surface population of two alkoxides bound to the same Ti cation must be exceedingly small. TPD experiments have shown strong steric barriers to accommodation of pairs of 2-propoxide ligands on individual surface cations (6, 21, 47). We conclude that 2-propanol could not effectively compete with hydroxyls for binding to a Ti cation which already contains one bound alkoxide.

One of the key results from previous studies on oxide single crystals and powders is that both dehydrogenation and dehydration of alcohols occur via initial dissociative adsorption to form alkoxides (6, 19–21). The involvement of hydroxyl groups in the dehydrogenation of 2-propanol via adsorbed alkoxides is also consistent with previous studies of alcohol decomposition on single-crystal and powder samples from this laboratory (6, 21, 47). In TPD experiments with 2-propanol adsorbed on oxidized single crystal TiO_2 surfaces in UHV, little or no dehydrogenation to form acetone was observed, but substantial dehydration did occur (21). On oxidized polycrystalline powders of anatase and rutile TiO_2, TPD of adsorbed 2-propanol resulted in the formation of small amounts of dehydrogenation product, with dehydration being the main decomposition route (6, 47). Both of these experiments can be considered to have been performed in an inert (i.e., UHV or helium) environment. In both studies, substantial amounts of 2-propanol were desorbed at 350–550 K; this desorption feature has been ascribed to a reaction between hydroxyls and alkoxides, resulting in the re-formation of the alcohol which desorbs (6, 21). This pathway effectively eliminates hydroxyls which may be bonded with alkoxides to the same Ti cation during the TPD experiment. The hydroxyl-mediated dehydrogenation route does not proceed at measurable rates until higher temperature ($\approx$475 K). Therefore, little or no dehydrogenation via this route would take place during the low temperature portion of the TPD process. Similar arguments can be made to explain the lack of an effect of hydroxyl coverage on the high temperature decomposition routes of ethanol found on a TiO_2 single crystal (43) and rutile TiO_2 powder (42). A sufficient population of hydroxyls added at room temperature does not survive to high temperature during the TPD process to produce a measurable effect; the hydroxyls either combine with alkoxides to desorb alcohol, or disproportionate to form water.

Above 525 K in the TPD experiment, water or hydroxyls are generated, as the dehydration of the alkoxide to propylene begins to occur. These hydroxyls can participate in the α-H abstraction step if they are bound to a Ti cation also containing an alkoxide, resulting in dehydrogenation to acetone. This step is also in competition with a surface hydroxyl disproportionation step to form water. The desorption rate maxima of all three species, propylene, acetone and water, are observed in TPD within the same temperature region, 550–580 K, as would be expected for the above described processes.

In TPD of 2-propanol adsorbed on TiO_2 powders, readsorption of 2-propanol desorbing in the 350–550 K range can occur. This readsorption, if it is dissociative, would almost certainly ensure that the hydroxyl and alkoxide formed are bound to the same Ti cation. At the upper end of this temperature range, the α-H abstraction process can proceed at measurable rates, and dehydrogenation should be observed. In fact, the desorption trace for acetone from anatase and rutile TiO_2 powders shows an asymmetric leading edge, indicating desorption of acetone is occurring at measurable rates as low as 450 K. This is substantially lower than the temperature at which the desorption rate of propylene becomes measurable, leading to a high predicted selectivity to dehydrogenation. Results from the steady-state experiments confirm this observation: at temperatures below 523 K, the selectivity to acetone approaches 100% in both inert and air carrier experiments.

The increased rate of dehydrogenation observed with increasing oxygen partial pressure is also consistent with the proposed hydroxyl-mediated α-H abstraction step. As the partial pressure of O_2 is increased, less H_2 and more H_2O are observed in the effluent of the reactor. These higher concentrations of H_2O will act in the manner described above for increasing conversion in an inert carrier or the water addition experiments. This is consistent with the previously discussed strong similarities in the observed effect of both water and O_2 addition on the 2-propanol decomposition kinetics: O_2 is not directly responsible for higher dehydrogenation rates, yet assists dehydrogenation in some fashion.

The mechanism by which O_2 produces higher effective concentrations of water and thus higher dehydrogenation rates, while having no effect on the dehydration rate (see Fig. 9), is difficult to establish unequivocally from the present results. The rate of 2-propanol consumption is also observed to increase with the addition of O_2 to the carrier gas. A most likely effect of the presence of O_2 would be to replace any surface oxygen consumed during the steadystate reaction. To explain these effects, we propose that the role of O_2 is to replace the most labile surface oxygen surface species which are either coordinated or consumed during steady-state reaction. Oxygen adsorption provides additional active sites for adsorption and subsequent dissociation of the alcohol, increasing the rate of 2-propanol consumption. Alcohol dissociation, in turn, increases the density of surface hydroxyl groups, thus increasing the rate of OH-mediated α-H abstraction, promoting the dehydrogenation route. This role of O_2 is consistent with the observed kinetics: the reaction order with respect to 2-propanol is not zero, suggesting the rate would be enhanced by an increased alcohol adsorption rate and/or higher alkoxide concentration.

CONCLUSIONS

Selectivity in the decomposition of 2-propanol on oxidized anatase TiO_2 has been shown to be a function of not only the surface properties of the oxide, but also the reaction conditions employed. Important experimental parameters include reaction temperature, alcohol partial pressure, the oxidizing nature of the carrier gas, and the quantity of surface hydroxyl groups. The rate of dehydrogenation is particularly influenced by these reaction parameters, while the rate of dehydration is much less affected. Many of the apparently contradictory kinetics results from previous steady-state investigations can be reconciled by taking into account this strong dependence of the dehydrogenation rate on reaction conditions. Likewise, comparisons between steady-state and temperature-programmed desorption results are quite favorable when the experiments have been performed under similar conditions. Especially important for these comparisons are steady-state kinetics data obtained at low conversion to approximate as closely as possible the single-turnover events of TPD.

Acid sites on metal oxides, often associated with hydroxyl groups, have been suggested to be responsible for dehydration and, in a concerted fashion with basic sites, dehydrogenation in alcohol decomposition (27). In contrast to this conventional wisdom, the present results demonstrate that surface hydroxyl groups are directly involved in the *dehydrogenation* of 2-propanol on TiO_2, while the quantity of hydroxyls had no impact on the dehydration rate. This suggests that the notion of acid–base properties of metal oxides controlling the decomposition selectivities of alcohols bears little relationship to the actual behavior of 2-propanol on TiO_2. The use of such probe reactions as simple diagnostics of surface acid–base properties must therefore be approached with considerable caution.

While it is tempting to generalize these findings to the decomposition of 2-propanol on other basic metal oxides, the complex dependence of the reaction selectivity on experimental variables such as temperature, carrier gas and water content make such generalizations difficult. For example, we have found that the selectivity-enhancing effect of water is observed only above 525 K when 2-propanol is reacted on the rutile polymorph of TiO_2 (48). Such results illustrate the surprising synergistic effects of experimental variables which are often overlooked in heterogeneous catalysis research.

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